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VITREOUS AND GLASS CERAMIC MATERIALS BASED ON GLAUCONITE-BEARING ROCKS

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The possibility of using glauconite-bearing sedimentary rocks from Belarus in the form of glauconite sand and concentrated glauconite as aluminosilicate materials is established. The main physicochemical properties of the synthesized materials are identified, and the color characteristics of glasses and formation specifics of the structure and phase composition of glaze coatings and glass ceramic materials are investigated.

In the past decades Belarus geologists have discovered new deposits of mineral materials suitable for extensive use in the glass industry. A promising variety is represented by the glauconite-bearing rock from the Dobrush and Karpovtsy deposits, which is an aluminosilicate material including SiO_2, Al_2O_3, CaO, MgO, R_2O, Fe_2O_3 + FeO, as well as TiO_2, SO_3, and P_2O_5 impurities.

The presence of up to 9.2% (here and elsewhere wt. %) iron oxides in glauconite-bearing rocks and up to 25.5% in concentrated glauconite makes it possible to produce tinted glass and vitreous coatings, as well as glass-ceramic materials (rock glass ceramics and stone casting).

Glauconite sand from the Dobrush and Karpovtsy deposited has been approved as aluminosilicate material in melting industrial glasses that contain (%): 72.0 – 73.3 SiO_2, 1.0 – 2.0 Al_2O_3, 10.0 – 10.5 (CaO + MgO), 13.5 – 15.0 (Na_2O + K_2O). All materials used for the synthesis of glasses except for soda ash are minerals from Belarus deposits. The quantity of glauconite-bearing materials in the batch varies from 10 to 65%. The processes of preliminary treatment of glauconite and quartz sands are similar.

Glasses were melted in a flame batch furnace at a temperature of 1450 ± 10°C. The temperature rise rate is 200 – 300 K/h, and the exposure at the maximum temperature is 2 h. The obtained glasses have no inclusions and are homogeneous.

In their physiochemical properties (density, water resistance, microhardness, compression strength, and CLTE), the experimental glasses are not inferior to industrially produced compositions and are reproduced when using different samplings of mineral materials. Upon introducing 1% iron oxide converted to Fe_2O_3, the dilatometric curves recorded with a DIL 402 PC dilatometer from the NETZSCH Company exhibit a decrease by 2 – 4°C in the vitrification temperature of experimental glasses and 10 – 12°C decrease in the softening temperature. The crystallization capacity of glasses estimated based on the data of gradient heat treatment data decreases, as the content of iron oxides in glasses increases.

The color range of experimental glasses is represented by different shades of light blue, blue-green, and green colors. Glass tinting is related to the introduction of iron oxides (0.5 – 1.6 and 1.0 – 2.2% introduced via glauconite sand from the Karpovtsy and Dobrush deposits, respectively).

The spectral characteristics of glass samples 4 mm thick are registered using a SF-26 spectrophotometer in the wavelength range of 350 – 1200 nm. They depend on the overall content of iron oxides in glasses and the $Fe^{2+} : Fe^{3+}$ ratio varying from 0.15 to 0.30. The $Fe^{2+} : Fe^{3+}$ ratio is determined in accordance with the method in [1] based on optical density parameters for the wavelengths of 380 and 1050 nm, i.e., the respective absorption maximums for Fe^{3+} and Fe^{2+} ions.

Figure 1 shows the transmission spectra of glasses produced using glauconite sand from the Karpovtsy deposit. Under neutral melting conditions the dominant wavelength in the transmission spectrum of light blue and blue-green glasses is 490 – 500 nm. The light-blue and blue shades in glass tinting are determined by the increased content of structural groups $[Fe^{2+}O_{6/2}]$. As the content of iron oxides increases, the integral light transmission of glasses regularly decreases to approximately 35% for 2% iron oxides. Under oxidizing conditions the tinting of glasses varies from blue-green tones to saturated green tones (the $Fe^{2+} \rightleftarrows Fe^{3+}$ equilibrium shifts to the right). The shift of the transmission maximum to the wavelength range of 560 nm is related to the prevalence of structural groups $[Fe^{3+}O_{4/2}]$.

The introduction of a component with a high reducing factor (coal) into iron-bearing glass batches modifies the tinting mechanism: apart from ionic color centers, molecular color centers emerge as well: iron sulfide FeS and, possibly,

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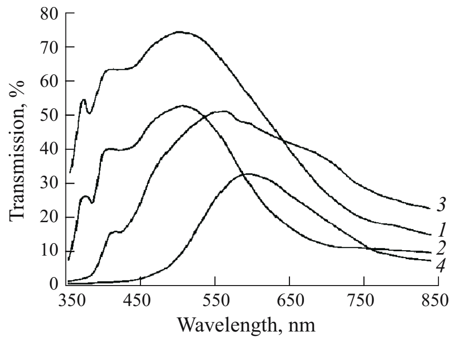

Fig. 1. Transmission spectra of tinted glasses: *1*) light blue; *2*) blue-green; *3*) green; *4*) brown.

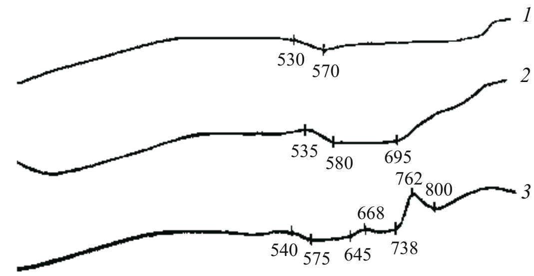

Fig. 2. Derivatograms of glaze glasses: *1*) clear; *2*) liquating; *3*) crystallizing.

amber chromophore $FeSO_3$ that has a high absorbing capacity in the wavelength range of 400 nm. This is responsible for yellow-brown hues in the glass tint and a low transmission in short-wave spectrum range under integral light transmission of 20 – 25%.

It should be noted that when glauconite sand from the Dobrush deposit is used, the glass tint is inhomogeneous: yellow hues related to the formation of iron sulfide are formed. In contrast to glauconite sand from the Karpovtsy deposit, the chemical composition of Dobrush sand has a higher content of SO_3 (up to 1%). Accordingly, it is advisable to use this sand for intensely colored yellow-brown container glasses that provide a high level of protection to food and drinks from the undesirable effect of ultraviolet radiation.

Tinting glass with complex colorants using iron oxides makes it possible to significantly expand the color range of glasses based on glauconite sand. Using the combination of colorants Fe_2O_3 (FeO) – Se – CoO, we have obtained samples of spectrally complex color shades (bronze, smoky, gray-green, etc.). The integral light transmission of such glasses is 35 – 48%.

Thus, the physicochemical and optical properties of glasses obtained using glauconite-bearing sedimentary rocks from the Republic of Belarus suggest that these materials can be used for the production of tinted glass products that do not have to meet high requirements on light transmission. This is primarily true of green and brown container glass. After adding complex colorants, it is possible to produce glasses of an expanded color range to be used in the production of figured glass sheets and glass blocks.

The synthesis and study of vitreous coatings have been performed on the basis of glasses containing (%): 47.3 – 62.6 SiO_2, 4.0 – 6.9 Al_2O_3, 5.0 – 20.0 B_2O_3, 6.2 – 14.0 R_2O, 2.0 – 14.5 RO, 2.7 – 14.8 Fe_2O_3 (R_2O — Na_2O, K_2O; RO — CaO, MgO, BaO, and ZnO). The raw materials were natural sand and concentrated glauconite from the Karpovtsy and Dobrush deposits, boric acid, soda ash, chalk, magnesium and barium carbonates, zinc oxide, and technical alumina. Vitreous coatings have been obtained based on optimum glass compositions obtained by moist fine milling adding 5 – 7% refractory clays with a subsequent deposition of the suspension on a ceramic substrate. The thermal treatment of samples was carried out within a temperature interval of 850 – 1050°C with a 30-min exposure at the maximum temperature.

It is established that the spreading capacity of glazes based on glauconite-bearing materials depends on the crystallization and liquation processes. The opacification of vitreous coatings bearing up to 4.5% Fe_2O_3 is ensured by a joint introduction of CaO and MgO due to liquation separation. To intensify the liquation process, at least 1.6% MgO should be introduced into the glass composition. When the glass contains at least 10% iron oxide, the crystallization of iron-bearing phases (hematite and magnetite) takes place. Figure 2 shows derivatograms of optimum glaze glass compositions that are used to form clear, liquating, and crystallizing coatings.

Glasses containing up to 6.8% iron oxides fired in the temperature interval of 850 – 1050°C form pale green and greenish-gray glaze coatings. With a 10% or more Fe_2O_3 content coatings are tinted in various shades of brown.

The color parameters of iron-bearing glazes are determined by the coordination state of iron ions and depend on the molar ratio $(RO + R_2O)/(Al_2O_3 + B_2O_3 + Fe_2O_3)$. Under an excess of $(RO + R_2O)$ oxides, iron ions, similarly to aluminum and boron ions, form tetrahedral oxygen complexes $[Fe^{3+}O_{4/2}]^{-}R^{+}$ and $[Fe^{3+}O_{4/2}]^{-}_{2}R^{2+}$ and replace silicon in the glass structure. Glass compositions with the molar ratio $(RO + R_2O)/(Al_2O_3 + B_2O_3 + Fe_2O_3) > 1.15$ typically exhibit the tetrahedral coordination of Fe^{3+} ions and the octahedral coordination of Fe^{2+} ions. Glass compositions with the molar ratio $(RO + R_2O)/(Al_2O_3 + B_2O_3 + Fe_2O_3) < 1.15$ typically have Fe^{3+} ions in the octahedral coordination. Iron ions in the bivalent six-coordination state impart a bluish-green or blue color to glass. In the trivalent state they produce a yellowish-green or a yellow shade [2], which is lighter-colored in the presence of groups $[Fe^{3+}O_{4/2}]$ and transforms into a brown color with the formation of groups $[Fe^{3+}O_{6/2}]$.

The formation of a brown glaze coating is caused by the supersaturation of the melt by iron oxides and their partial transition into a crystalline phase. When the composition contains over 10% Fe_2O_3, the cations Fe^{3+} existing in the octahedral coordination during glass melting pass into the melt

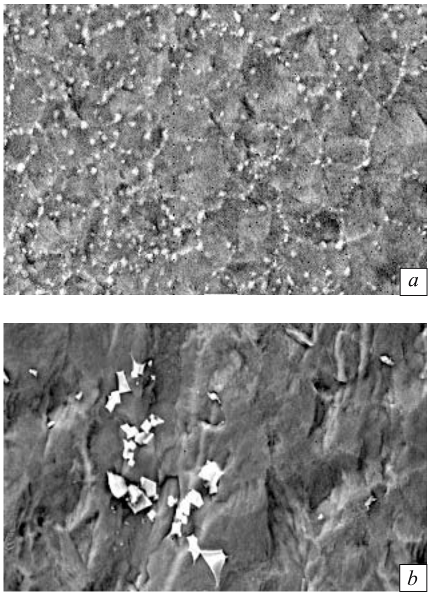

Fig. 3. Electron microscope photos of the surface of glass (*a*) and rock glass ceramics (*b*).

(1450°C). When a glaze coating is fused at a temperature of 740 – 800°C, ferrous phases (hematite and magnetite) are crystallized.

Structural modifications occurring in glasses with an increasing content of iron oxides were investigated using the IR spectroscopy method. The IR spectra of iron-bearing glasses have clearly expressed bands in the range of 1400 – 1405, 1058 – 1074, 780 – 800, 695 – 702, and 460 – 468 cm^{-1}. The specific feature of the IR spectra is the shift of the absorption band in the range of 900 – 1100 cm^{-1} and its decreasing intensity with increasing content of iron oxides. This may be caused by a decreased polymerization of groups consisting of $[SiO_4]$ tetrahedra and their increased degree of differentiation by the types of structural complexes. The emergence of low-intensity maxima at 574 – 580 cm^{-1} may point to atom vibrations in the Me – O bonds [2].

The research performed made it possible to identify the composition of glasses for the synthesis of clear or opacified vitreous glaze coatings. Thus, compositions containing (%): 47.8 – 60.0 SiO_2, 4.0 – 5.7 Al_2O_3, 10.0 – 20.0 B_2O_3, 6.2 – 14.0 R_2O, 8.3 – 14.3 RO, and 2.7 – 7.0 Fe_2O_3 synthesized on the basis of glauconite-bearing rock can produce both clear and opacified coatings, whose color range varies from yellowish-green to greenish-gray. The microhardness of these coatings is 4300 – 6600 MPa, heat resistance 110 – 230°C, CLTE (50.82 – 68.82) × 10^{-7} K^{-1}, luster 54 – 81%, and fusing temperature 800 – 1050°C.

The composition range containing (%): 47.30 – 53.30 SiO_2, 5.27 – 6.89 Al_2O_3, 10.00 – 20.00 B_2O_3, 8.70 – 10.00 R_2O, 3.25 – 8.70 RO, and 11.79 – 14.80 Fe_2O_3 based on concentrated glauconite makes it possible to obtain glaze coatings with a good spreading capacity and a range of brown shades. The microhardness of these coatings is 4300 – 6000 MPa, heat resistance 230 – 260°C, CLTE (61.5 – 65.0) × 10^{-7} K^{-1}, luster 67 – 79%, and fusing temperature 950 – 1050°C.

In earlier studies rock glass-ceramics and stone casting were synthesized based on granitoids and metadiabase subject to correction in the quantities of calcium and magnesium oxides, which together with SiO_2 are the main components ensuring the formation of pyroxene solid solutions [3, 4]. These materials have high chemical and wear resistance, which is typical of pyroxene glass ceramics.

We have investigated the synthesis of pyroxene rock glass ceramics and stone casting based on glauconite-bearing materials that have an increased content of iron oxides (concentrated glauconite) or silicon dioxide (glauconite sand).

In the experiment we decreased the number of components in the system by using natural minerals, approaching as much as possible the optimum compositions of known pyroxene glass ceramics.

Based on the chemical composition of glauconite-bearing materials, we obtained two series of glasses based on batches containing (%): 60 – 100 concentrated glauconite, 10 – 100 glauconite sand, and 0 – 15 dolomite. No crystallization stimulator was introduced into the batches of the first series, whereas chromium oxide in the amount of 1% (above 100%) was used in the second series.

The estimated chemical composition of experimental glasses (%): 49.42 – 81.05 SiO_2, 0.26 – 0.74 TiO_2, 3.44 – 9.52 Al_2O_3, 3.47 – 21.29 Fe_2O_3, 1.91 – 9.72 CaO, 2.01 – 9.72 MgO, 1.51 – 7.38 R_2O.

Analysis of the results of synthesis of melts and glasses indicates that the high content of SiO_2 in glauconite sand makes it virtually unsuitable for producing effective glass melts, whereas concentrated glauconite is the most acceptable component. The optimum batch composition including 85% concentrated glauconite, 15% dolomite, and 1% Cr_2O_3 produced a melt suitable for rock glass ceramics or for stone casting. The glass is more prone to volumetric crystallization, which is caused by the presence of a substantial (19.21%) content of Fe_2O_3 causing the formation of spinellides already at the stage of glass melt cooling. Magnesioferrite $MgFe_2O_4$ is formed when Cr_2O_3 is not used, and chromite $FeCr_2O_4$ is formed when Cr_2O_3 is used. These phases act as crystallization centers of the main mineral phases: augite (Ca, Mg, Fe^{2+}, Fe^{3+}, Ti, Al)[(Si, Al)$_2$O$_6$], hedenbergite Ca(Fe^{3+}, Mg)[Si_2O_6], and esseneite $CaFe_3AlSiO_6$.

Glass of the optimum composition was used to produce samples of rock glass ceramics and stone casting; the heat treatment temperature in the synthesis of rock glass ceramics was 850°C and in stone casting 810 – 820°C, with respective exposures of 1 and 0.5 h.

Study of the microstructure of glass and glass ceramic samples using a JEOL JSM 5610 LV scanning microscope (× 1000) demonstrates (Fig. 3) that the cooled sample already contains crystalline phases represented by pyroxenes: augite, hedenbergite, and essenesite, which are not yet morphologically shaped. This is a distinctive structural feature of

the obtained samplers caused by the presence of the specified crystalline phases. The completion of the crystallization process and the final shaping of the crystalline structure occur at a temperature of 850°C. The crystalline formation of a typical hexahedral habitus can be attributed to the spinellide type.

No perceptible differences were identified in the structure of rock glass ceramics and stone casting obtained from the optimum batch composition, which is presumably due to the high propensity of the melt and the glass for crystallization. Consequently, their physicochemical and mechanical properties are similar as well: density 3005 – 3014 kg/m^3, microhardness 9260 – 9580 MPa, and chemical resistance in 1-N HCl equal to 99.74 – 99.82%.

Thus, pyroxene glass ceramic materials synthesized on the basis of concentrated glauconite are competitive with regard to known materials obtained on the basis of melted basalt, metadiabase, and granitoides.

The studies performed have confirmed the advisability of using local glauconite-bearing materials to produce tinted glasses and glazes, as well as glass-ceramic materials.

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